

(43) Date of A publication 25.08.1993

(21) Application No 9302603.7

(22) Date of filing 10.02.1993

(30) Priority data

| | | |
|---------------|-----------------|---------|
| (31) 04303825 | (32) 13.11.1992 | (33) JP |
| 04357201 | 21.12.1992 | |
| 04023973 | 10.02.1992 | |

(51) INT CL⁵

C08F 8/06 212/08 220/38

(52) UK CL (Edition L)

C3J JAK JAR JCA

C3P PDIF

C3W W209 W211 W215 W223 W225 W226 W227
W302

U1S S1391 S3009

(71) Applicants

Toagosei Chemical Industry Co. Ltd.

(Incorporated in Japan)

14-1 Nishi Shimbashi, 1-chome, Minato-ku, Tokyo,
Japan

Toyota Jidosha Kabushiki Kaisha

(Incorporated in Japan)

1 Toyota-cho, Toyota-shi, Japan

Toyoto Technological Institute

(Incorporated in Japan)

12-1 Hisakata-2-Chome, Tenpaku-Ku, Nagoya-Shi,
Japan

(56) Documents cited

GB 1526301 A GB 1283087 A EP 0096459 A2

(58) Field of search

UK CL (Edition L) C3J JAK, C3P PDIF
INT CL⁵ C08F

(72) Inventors

Mitsuru Nagasawa

Kazuyuki Kuwano

Takeshi Kawakami

Mamoru Suglura

Hiroshi Hibino

Shiro Kojima

Kishiro Azuma

(74) Agent and/or Address for Service

D Young & Co

21 New Fetter Lane, London, EC4A 1DA,
United Kingdom

(54) A process for producing a polymer having excellent weatherability

(57) A process for producing a polymer of excellent weatherability, which comprises reacting a polymer having a thioether bond, with a peroxide to oxidize the sulphur atom in the bond to convert it into a sulphone. In one process the sulphone-containing polymer is reacted with an unsaturated compound to form a macromolecule which may be copolymerised with another monomer. In another process the thioether-containing polymer may be reacted with an unsaturated compound to form a macromolecule which is copolymerised and then oxidised.

A PROCESS FOR PRODUCING A POLYMER
HAVING EXCELLENT WEATHERABILITY

The present invention relates to a process for producing a
5 polymer, and particularly, but not exclusively a (meth)acrylic acid
ester type polymer of excellent weatherability, suitable for use in
coatings, paints, etc. A coating composition containing, as a main
component, a polymer obtained by the present process is suitable for
the coating of metals, plastics, wood, etc., and particularly, but not
10 exclusively, the coating of automobiles and household electrical
appliances.

Organic solvent-based acrylic coatings have generally been used
for coating automobiles, household electrical appliances, etc. because
of their excellent weatherability and appearance. Recently, however,
15 it has become a task of the coating industry, due to environmental
protection reasons, to provide organic solvent-based acrylic coatings
having a high solid content.

A high solid content can be achieved by decreasing the molecular
weight of a resin used in coatings. For example, Journal of Coating
20 Technology Vol. 59, No. 749, June 1987 proposes using in high solid
coatings a polymer having a number-average molecular weight of 650-
3,100, which is obtained by copolymerizing an alkyl acrylate, styrene,
acrylic acid, etc. in the presence of 3-mercaptopropionic acid.

Other methods for achieving a high solid content include using a
25 branched-chain polymer as a resin for coating, and the use of the
following branched-chain polymer has been proposed:

For example, according to Japanese Patent Application Kokai No.
4-103610, a branched-chain polymer obtained by copolymerizing a
radical-polymerizable macromolecular monomer containing, as the
30 skeleton, a polymer obtained by radical polymerization of an alkyl
(meth)acrylate, etc. in the presence of a mercaptan, with another
monomer, gives a low-viscosity solution even at a high solid content
and is therefore suitable as a resin for high-solid coating.

An example of a process for the synthesis of the above radical-
35 polymerizable macromolecular monomer is described below in detail.

A radical-polymerizable monomer is polymerized in the presence of
a mercaptan having a thiol group and a carboxyl group such as

thioglycolic acid or mercaptopropionic acid to obtain a polymer having a number-average molecular weight of 1,000-20,000 and having a carboxyl group at one end of the molecule. Then, the polymer is reacted with a monomer having an addition-reactive group such as glycidyl methacrylate or the like to obtain a macromolecular monomer having a methacryloyl group at one end of the molecule.

The polymer or macromolecular monomer obtained by radical polymerization using a mercaptan as a chain transfer agent, however, has had the problem of having inferior weatherability, because the polymer or macromolecular monomer contains a thioether bond which is easily deteriorated by ultraviolet rays. Branched-chain polymers containing said macromolecular monomer as a component have had the same problem.

We have now found it possible to improve the weatherability of a polymer composed mainly of a (meth)acrylic acid ester monomer or the like and having a thioether bond, obtainable by the above process.

According to the present invention there is provided a process for producing a polymer (including a macromolecular monomer) of excellent weatherability, which comprises reacting a polymer having a thioether bond with a peroxide to oxidize the sulfur atom in the thioether bond to convert it into a sulfone.

Polymers having a thioether bond which may be used in the present invention include, for example, straight-chain or branched-chain polymers having a number-average molecular weight of 500-20,000 and having a thioether bond, and a branched-chain polymer obtained by copolymerization of a macromolecular monomer having a thioether bond with another monomer.

According to a first aspect of the present invention there is provided a process for producing a polymer of excellent weatherability, which comprises polymerizing an ethylenically unsaturated monomer in the presence of a mercaptan to obtain a straight-chain or branched chain polymer having a number-average molecular weight of 500-20,000 having a thioether bond and then reacting the polymer with a peroxide to oxidize the sulfur atom in the thioether bond to convert it into a sulfone.

According to a second aspect of the present invention there is provided a process for producing a macromolecular monomer of excellent

weatherability, which comprises the following steps [a] to [c]:

- [a] a step of polymerizing at least one ethylenically unsaturated monomer in the presence of a mercaptan having a thiol group and a reactive group in the molecule,
- 5 [b] a step of reacting the polymer obtained in the step [a], with a peroxide to oxidize the sulfur atom in the thioether bond present in the polymer to convert it into a sulfone, and
- 10 [c] a step of reacting the polymer obtained in the step [b], with a compound having a functional group which is addition-reactive with the reactive group present at one end of the polymer, and an ethylenically unsaturated bond, to obtain a macromolecular monomer of excellent weatherability.

According to a third aspect of the present invention there is provided a process for producing a branched-chain polymer of excellent weatherability, which comprises the following steps [d] to [g]:

- [d] a step of polymerizing an ethylenically unsaturated monomer in the presence of a mercaptan having a thiol group and a reactive group in the molecule,
- 20 [e] a step of reacting the polymer obtained in the step [d] with a compound having a functional group which is addition-reactive with the reactive group present at one end of the polymer, and an ethylenically unsaturated bond, to obtain a macromolecular monomer,
- 25 [f] a step of copolymerizing the macromolecular monomer having an ethylenically unsaturated bond at one end of the molecule, obtained in the step [e] with another monomer to synthesize a branched-chain polymer, and
- 30 [g] a step of reacting the branched-chain polymer obtained in the step [f] with a peroxide to oxidize the sulfur atom in the thioether bond present in the branched-chain polymer to convert it into a sulfone.

Various preferred features and embodiments of the present invention will now be described by way of non-limiting example.

The mercaptan usable in the first aspect of the present invention may include, for example, butyl mercaptan, hexyl mercaptan, octyl mercaptan, lauryl mercaptan, mercaptoacetic acid, β -mercaptopropionic acid, β -mercaptoethanol, thioglycerol and thiomalic acid.

In the first aspect, the molecular weight of the polymer is 500-20,000 in terms of number-average molecular weight, as mentioned above, and is controlled by the amount of the mercaptan used. That is, the amount of the mercaptan used, which gives rise to a polymer having a number-average molecular weight of 500, is 50 moles per 100 moles of the total monomers fed, and the mercaptan amount corresponding to a polymer having a number-average molecular weight of 20,000 is 0.3 mole per 100 moles of the total monomers fed.

A polymer having a number-average molecular weight of more than 20,000 requires, for its production, a very small amount of the mercaptan. In this polymer, therefore, the reduction in weatherability due to the thioether bond may be negligible.

Ethylenically unsaturated monomers, which can be used in the first aspect of the present invention, include (meth)acrylic acid esters, such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, stearyl (meth)acrylate, behenyl (meth)acrylate, isobornyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate and the like; unsaturated carboxylic acids such as (meth)acrylate acid, maleic anhydride, itaconic acid and the like; styrene; α -methylstyrene; vinyl acetate; and acrylonitrile. Methacrylic acid esters are preferable in view of the weatherability of the polymer obtained.

As for the polymerization method, solution polymerization is preferable, and a polymerization solvent such as toluene, xylene, methyl, isobutyl ketone or the like can preferably be used. As the polymerization initiator, a radical-generating compound such as an azo compound, a peroxide compound or the like can be used.

Using the above polymerization a polymer having a number-average molecular weight of 500-20,000 can be obtained having a thioether bond derived from the mercaptan, at one end of the molecule.

Then, the polymer is reacted with a peroxide to oxidize the sulfur atom in the thioether bond present in the polymer to convert it into a sulfone.

In the above oxidation, it is possible to use the organic solvent solution obtained in the polymerization, as it is, or to isolate the polymer from said solution, redissolve the polymer in an organic

solvent such as methylene chloride, toluene, butyl acetate or the like and use the resulting solution.

Examples of preferred peroxides include organic peracids such as perbenzoic acid, m-chloroperbenzoic acid, peracetic acid, perhexanoic acid and the like; hydroperoxides such as tert-butyl hydroperoxide, cumene hydroperoxide and the like; and inorganic peroxides such as hydrogen peroxide, potassium persulfate, oxone, magnesium monoperoxyphthalate, ozone and the like. Organic peracids and inorganic peroxides are preferable, and particularly preferable are m-chloroperbenzoic acid, hydrogen peroxide and ozone.

A catalyst may be used in combination with the peroxide. An example of the preferable catalyst is phosphotungstic acid.

In the oxidation using the peroxide, the sulfur atom in the thioether bond in the polymer to be oxidized is oxidized in two stages. In the first-stage of the oxidation of the sulfur atom, the thioether bond is converted into a sulfoxide and, in the second stage of the oxidation of the sulfur atom, the sulfoxide is converted into a sulfone. As a result of the two-stage oxidation, the polymer obtained has improved weatherability.

The amount of the peroxide used should be at least twice the equivalent of thioether bond contained in the polymer to be oxidized. When the amount of the peroxide used is less than twice the equivalent, a part of the sulfur atom in the thioether bond may only be oxidized as in the first-stage of the oxidation (resultantly, a part of the thioether bond may be converted only into a sulfoxide and not converted into a sulfone), and the polymer obtained may not have sufficient weatherability.

When the peroxide used is a powder of an organic peracid (e.g. m-chloroperbenzoic acid), the organic peracid may be added to a solution of the polymer to be oxidized, as it is, or the peroxide may be added in the form of a solution dissolved in an organic solvent.

When the peroxide used is a water-soluble inorganic peroxide (e.g., hydrogen peroxide), it is preferable that the peroxide be added to a solution of the polymer to be oxidized, in the form of a solution dissolved in water. The two solutions can be stirred and efficiently brought into contact, and then the aqueous layer and the organic layer can be separated from each other by, for example, centrifuging or the

like.

When ozone is used, it is preferable that the ozone is blown into a solution of the polymer to be oxidized, to bubble the solution.

The reaction temperature is preferably about 0°C to room temperature when a peroxide of high oxidizing power, such as *m*-chloroperbenzoic acid, ozone or the like is used, and about 50-80°C when a peroxide of intermediate oxidizing power, such as hydrogen peroxide or the like is used. The reaction time is generally about 1-20 hours.

The progress of the oxidation can be determined by measuring, by ¹H-NMR, the chemical shift of the hydrogen atoms in the CH₂ adjacent to the sulfur atom in the polymer to be oxidized.

The polymer of excellent weatherability obtained in the second aspect of the present invention can be used in one component air-drying coatings, and curing type coatings which include a curing agent.

For use in air-drying type coatings, a polymer having a number-average molecular weight of 5,000-20,000 is preferable.

For use in curing type coatings, a polymer having a number-average molecular weight of 500-15,000 having, in the molecule, a functional group such as hydroxyl group, carboxyl group, amino group or the like is preferred. Curing agents which may be used in combination with the polymer, include polyisocyanate compounds, aminoplast resins, etc.

The second aspect of the present invention will now be described in greater detail.

In the second aspect directed to a process for producing a macromolecular monomer, there is obtained, in the step [a], a polymer having a reactive group at one end of the molecule, by using, as a chain transfer agent, a mercaptan having a reactive group and a thiol group in the molecule. The polymer preferably has a number-average molecular weight of 1,000-20,000.

Specific examples of the reactive group in the mercaptan used in the step [a] are a carboxyl group and a hydroxyl group. Examples of a mercaptan having such a reactive group include mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid and 2-mercaptoethanol.

The amount of the mercaptan used is preferably about 1-30 moles, more preferably about 5-20 moles per 100 moles of total monomer used in

the polymerization.

Monomers which may be used in the step [a], include, for example, methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl
5 (meth)acrylate, (meth)acrylonitrile, styrene and α -methylstyrene.

As the polymerization method, solution polymerization is preferable. The polymerization solvent, polymerization initiator, etc. used are basically the same as in the first aspect.

In the step [b], the sulfur atom in the thioether bond present in
10 the polymer obtained in the step [a] is oxidized with a peroxide to convert the thioether bond into a sulfone. The oxidation is conducted basically in the same manner as in the first aspect.

In the step [c], the polymer obtained in the step [b] is reacted with a monomer having a functional group addition-reactive with the
15 reactive group in said polymer and an ethylenically unsaturated bond (the monomer is hereinafter referred to as "functional group-containing monomer"), whereby a macromolecular monomer having an ethylenically unsaturated bond at one end of the molecule is obtained.

The functional group-containing monomer to be reacted with the
20 polymer obtained in the step [b], may be, for example, glycidyl methacrylate, glycidyl acrylate, methacrylic acid chloride, p-vinylbenzyl chloride and p-vinylaniline. Of these monomers, preferable are glycidyl methacrylate and glycidyl acrylate.

The reaction between the polymer and the functional group-
25 containing monomer is conducted preferably at an approximately equimolar ratio or at a molar ratio in which the latter is excessive. The reaction can be conducted in an organic solvent, and the reaction temperature is preferably about 60-120°C. An appropriate amount of a catalyst may be used if necessary.

30 By the above process there can be obtained a macromolecular monomer having, as a polymerizable group, an ethylenically unsaturated bond such as acryloyl group, methacryloyl group, vinylbenzyl group or the like.

The resulting macromolecular monomer contains no thioether bond.
35 Hence, for example, by copolymerizing the macromolecular monomer with another monomer, a branched-chain polymer containing no thioether bond can be obtained. The branched-chain polymer has excellent

weatherability and can be suitably used in coatings or paints.

The third aspect of the present invention will now be described in greater detail.

5 The steps [d] and [e] in the third aspect are the same as the steps [a] and [c] in the second aspect, respectively.

10 In the step [f], the macromolecular monomer obtained in the step [e] is copolymerized with another monomer to synthesize a branched-chain polymer containing said macromolecular monomers as the side chain. The branching degree of the branched-chain polymer is controlled by the proportions of the macromolecular monomer and the other monomer copolymerized. The higher the proportion of the macromolecular monomer, the higher the resulting branching degree of the branched-chain polymer.

15 A polymer having a higher degree of branching has a larger molecular weight and gives a solution of lower viscosity and therefore is better suited for use in high-solid coatings. The polymer for use in said coatings contain the macromolecular monomer unit in an amount of preferably about 40% by weight or more, more preferably about 55-99.5% by weight based on the total amount of constituent units.

20 The preferable weight-average molecular weight of the branched-chain polymer is about 5,000-30,000. When the weight-average molecular weight of the branched-chain polymer is less than 5,000, the resulting coating is inferior in durability. When the molecular weight is more than 30,000, the polymer gives a solution of high viscosity, which gives poor coatability.

25 The monomer to be copolymerized with the macromolecular monomer, may be, for example, alkyl (C_1 - C_{18}) (meth)acrylate, perfluoroalkyl (C_1 - C_{18}) (meth)acrylates, styrene, (meth)acrylonitrile, (meth)acrylic acid, maleic anhydride, 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, glycidyl (meth)acrylate, N-methylolacrylamide, N,N-dimethylamino ethyl (meth)acrylate and (meth)acryloyloxypropyltrimethoxysilane. In view of the excellent weatherability of the branched-chain polymer obtained, (meth)acrylic acid esters such as alkyl (meth)acrylates, hydroxyalkyl (meth)acrylates and the like are
35 preferable,

1 and alkyl (meth)acrylates such as methyl (meth)acrylate,
butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and the
like are particularly preferable.

5 In a preferred constitution of the branched-
chain polymer, the amount of the alkyl (meth)acrylate
monomer unit is about 60-80% by weight based on the total
amount of (1) the monomer units constituting the
macromolecular monomer and (2) the unit of the above
monomer copolymerized with the macromolecular monomer.

10 As the polymerization method, solution
polymerization is preferable. In the polymerization,
there can be used a polymerization solvent such as
toluene, xylene, methyl ethyl ketone, methyl isobutyl
ketone or the like.

15 As the polymerization initiator, there is
preferred an azo compound such as 2,2-azobisiso-
butyronitrile or the like, or an organic peroxide such as
benzoyl peroxide or the like. The preferable amount of
the initiator used is about 1-10 moles per 100 moles of the
20 total of the macromolecular monomer and the monomer
copolymerized therewith, and is about 1-3 moles when the
following chain transfer agent is used in combination.

In the step [f], it is preferable that a chain
transfer agent such as dodecyl mercaptan, mercapto-
25 ethanol, thioglycollic acid or the like be used. The
preferable amount of the chain transfer agent used is about 2-
15 moles per 100 moles of the total of the macromolecular
monomer and the monomer copolymerized therewith.

1 In the next step [g], the branched-chain
polymer obtained in the step [f] is reacted with a
peroxide in the same manner as in the step [b] of the
second aspect to oxidize the thioether bond in the
5 polymer, whereby a branched-chain polymer of excellent
weatherability is obtained.

The branched-chain polymer thus obtained gives
a resin solution of high solid content and yet low
viscosity. Moreover, the polymer has excellent weather-
10 ability. Hence, it can be very suitably used as a resin
for coatings.

The branched-chain polymer can be used in air-
drying type coatings. Also, when the polymer contains a
crosslinkable functional group such as carboxyl group,
15 hydroxyl group or the like, it can be used in heat-curing
type coatings by using it in combination with a crosslinking
agent such as aminoplast resin, polyisocyanate compound
or the like. The heat-curing type coating obtained by
the present invention is particularly suitable as a
20 coating for automobiles.

The present invention is hereinafter described
specifically by way of Examples and Comparative Examples.
Incidentally, the weatherability of each polymer
obtained in each Example or Comparative Example was
25 evaluated by the following method.

Each of the polymers obtained was made into a
toluene solution containing 30% of the polymer. The
solution was coated on a glass plate using a bar coater

1 and dried. The resulting film was forcibly deteriorated
at 83°C for 220 hours with no water sprayed, using a
sunshine weatherometer (hereinafter referred to as SWOM).
The coloring of the film after the above test was
5 examined visually.

Example 1

106 parts by weight of toluene was fed into a
flask equipped with a stirrer, a reflux condenser, a
dropping funnel, a thermometer and a nitrogen-inlet tube.
10 The toluene temperature was kept at 80-85°C with nitrogen
gas being introduced into toluene.

From the dropping funnel was continuously
dropped, in 3 hours, a mixture consisting of 10 parts by
weight of 2-hydroxyethyl methacrylate, 45 parts by weight
15 of butyl methacrylate, 10 parts by weight of styrene, 24
parts by weight of ethyl acrylate, 5 parts by weight of
methacrylic acid, 6 parts by weight of mercaptoacetic
acid and 2 parts by weight of azobisisobutyronitrile
(hereinafter referred to as AIBN). After the completion
20 of the dropping, the same temperature was kept for 2
hours and stirring was continued. Then, the polymeri-
zation reaction was completed.

After the polymerization, the average
conversion of the monomers used was measured by gas
25 chromatography to get 98%. The molecular weight of the
polymer obtained was measured by gel permeation chromato-
graphy on the basis of calibration with polystyrene

1 standard (hereinafter referred to as GPC) to get 1,500 in
terms of number-average molecular weight and 3,000 in
terms of weight-average molecular weight.

The polymer solution in toluene was added to an
5 aqueous methanol solution to precipitate the polymer.
The polymer was separated and then vacuum-dried at 40°C
to obtain a polymer A having slight stickiness.

10 parts by weight of the polymer A was
dissolved in 100 parts by weight of methylene chloride.
10 The resulting solution was kept at 0°C. Thereto was
added 8 parts by weight of m-chloroperbenzoic acid
(purity = 80%). The mixture was subjected to oxidation
reaction for 1 hour with stirring.

The relationship between the amount of the
15 thioether bond in the polymer and the amount of the
peroxide used was as follows.

Amount of thioether bond in polymer: 0.0064 mole

Amount of peroxide used: 0.037 mole

Ratio of peroxide to thioether bond: 5.8 times in
20 equivalent

The reaction mixture was washed with 200 parts
by weight of 10% aqueous sodium hydrogencarbonate
solution to remove the residual peroxide, after which
methylene chloride was evaporated to obtain an oxidized
25 polymer.

The polymer was made into a 30% toluene
solution. A coating film was formed using the solution
and evaluated for weatherability using SWOM. As a

1 result, the film was only slightly colored in yellow
after 220 hours and had excellent weatherability.

Example 2

10 parts by weight of the polymer A obtained in
5 Example 1 was dissolved in 100 parts by weight of
toluene. To the solution was added 5 parts by weight of
m-chloroperbenzoic acid (purity = 80%), and the mixture
was subjected to oxidation reaction at 20°C for 5 hours.
The amount of the peroxide used was 3.6 times the equiva-
10 lent of that of the thioether bond in the polymer.

From the resulting polymer was formed a coating
film in the same manner as in Example 1. The film was
evaluated for weatherability. As a result, the film
was only slightly colored in yellow and had excellent
15 weatherability.

Comparative Example 1

The polymer A obtained in Example 1 was
evaluated for weatherability as it was, without being
oxidized. As a result, the film prepared from the
20 polymer A was colored in brown.

Comparative Example 2

The polymer A and m-chloroperbenzoic acid were
reacted in the following proportions.

Amount of thioether bond in polymer: 0.0064 mole
25 Amount of peroxide used: 0.0093 mole

Ratio of peroxide to thioether bond: 1.5 times in equivalent

From the resulting polymer was formed a coating film. The film was evaluated for weatherability. As a result, the film was colored brown.

In Comparative Example 2, the amount of m-chloroperbenzoic acid used was short. Hence, the sulfur atom in the thioether bond in the polymer A was not completely oxidized and the thioether bond was not sufficiently converted into a sulfone. As a result, the resulting polymer had insufficient weatherability. As clear from this Comparative Example, a polymer having a thioether bond or a sulfoxide group has insufficient weatherability.

15 Example 3

To a mixed solvent consisting of 50 parts by weight of butanol and 56 parts by weight of xylene was dropwise added, in the same manner as in Example 1, a mixture consisting of 10 parts by weight of 2-hydroxyethyl methacrylate, 45 parts by weight of butyl methacrylate, 10 parts by weight of methacrylic acid, 20 parts by weight of styrene, 14 parts by weight of ethyl acrylate, 1 part by weight of mercaptoethanol and 2 parts by weight of AIBN, to conduct polymerization reaction.

25 By the above polymerization reaction was obtained a polymer B having a number-average molecular weight of 7,700 and a weight-average molecular weight of

1 16,400 as measured by GPC.

10 parts by weight of the polymer B was dissolved in 100 parts by weight of methylene chloride. The solution was kept at 0°C. Thereto was added 8 parts
5 by weight of m-chloroperbenzoic acid (purity = 80%). The mixture was subjected to oxidation reaction for 1 hour with stirring.

Amount of thioether bond in polymer: 0.0012 mole

Amount of peroxide used: 0.0093 mole

10 Ratio of peroxide to thioether bond: 7.7 times in equivalent

From the resulting polymer was formed a coating film. The film was evaluated for weatherability. As a result, the film was nearly colorless and had excellent
15 weatherability.

Comparative Example 3

The polymer B obtained in Example 3 was evaluated for weatherability as it was, without being oxidized. As a result, the film prepared from the
20 polymer B was colored in yellow.

Example 4

[Synthesis of macromolecular monomer]

106.2 parts by weight of toluene was fed into a flask equipped with a stirrer, a reflux condenser, a
25 dropping funnel, a thermometer and a nitrogen-inlet tube. The toluene temperature was kept at 80-85°C by stirring,

1 with nitrogen gas being introduced into toluene.

From the dropping funnel was continuously dropped, in 3 hours, a mixture consisting of 100 parts by weight of methyl methacrylate, 10.6 parts by weight of
5 mercaptoacetic acid and 2 parts by weight of AIBN, to react them. After the completion of the dropping, the reaction was continued further for 2 hours to obtain a toluene solution of polymethyl methacrylate having a carboxyl group at one end of the molecule.

10 The polymer had a number-average molecular weight of 1,500 and a weight-average molecular weight of 3,000. The amount of carboxyl group in the polymer was 37 mgKOH/g of polymer.

10 parts by weight of the polymer was dissolved
15 in 100 parts by weight of methylene chloride. To the solution was added 8 parts by weight of m-chloroperbenzoic acid. The mixture was subjected to reaction at 0°C for 1 hour. The reaction mixture was subjected to the same procedure after oxidation reaction as in Example
20 1, to separate an oxidized polymer from the reaction mixture.

The resulting polymer was reacted with glycidyl methacrylate in toluene. Glycidyl methacrylate was used in an amount of about 1.1 times in equivalent that of the
25 carboxyl group in the polymer. The reaction was conducted in the presence of hydroquinone monomethyl ether as a polymerization inhibitor and a quaternary ammonium salt as a catalyst, at 90°C for 6 hours.

1 After the reaction, the resulting polymer was
measured for acid value, which indicated that the degree
of conversion was 98.5%.

5 By the above reaction was obtained a macro-
molecular monomer having a methacryloyl group at one end
of the molecule.

[Synthesis of branched-chain polymer]

10 The above-obtained macromolecular monomer,
styrene and methyl methacrylate were used at a weight
ratio of 45:25:30. There was also used 8.4 mole %, based
on the total moles of the above polymerizable components,
of AIBN as a polymerization initiator. They were
subjected to polymerization reaction in toluene at 60°C
for 8 hours.

15 The resulting polymer had a number-average
molecular weight of 7,000 and a weight-average molecular
weight of 14,000 as measured by GPC.

 The polymer was evaluated for weatherability.
As a result, the film of the polymer gave no yellowing.

20 Comparative Example 4

 Methyl methacrylate was polymerized in the same
manner as in the step of [Synthesis of macromolecular
monomer] of Example 4, to obtain a polymethyl meth-
acrylate (number-average molecular weight = 1,500,
25 weight-average molecular weight = 3,000) having a
carboxyl group at one end of the molecule. The poly-

1 methyl methacrylate was reacted with glycidyl meth-
acrylate as it was, without being oxidized, whereby a
macromolecular monomer was synthesized.

The macromolecular monomer, styrene and methyl
5 methacrylate were copolymerized in the same manner as in
Example 4 to obtain a branched-chain polymer having a
number-average molecular weight of 7,000 and a weight-
average molecular weight of 14,000. The polymer was
evaluated for weatherability. As a result, the film
10 of the polymer was brown colored.

Example 5

The branched-chain polymer obtained in
Comparative Example 4 (a branched-chain polymer obtained
by copolymerizing a polymethyl methacrylate type macro-
15 molecular monomer, styrene and methyl methacrylate at a
weight ratio of 45:25:30) was oxidized with a peroxide as
follows.

24 parts by weight of the branched-chain
polymer was dissolved in 300 parts by weight of methylene
20 chloride. To the solution was added 14 parts by weight
of m-chloroperbenzoic acid. The mixture was subjected to
oxidation reaction at 0°C for 1 hour. Then, the oxidized
branched-chain polymer was separated from the reaction
mixture.

25 The branched-chain polymer was evaluated for
weatherability. As a result, the film of the polymer
gave no yellowing.

1 Example 6

A branched-chain polymer was produced by using a macromolecular monomer of 1,340 in number-average molecular weight and 2,600 in weight-average molecular weight, having a composition of methyl methacrylate/2-hydroxyethyl methacrylate = 80/20 (by weight %) and having a methacryloyl group at one end of the molecule.

The above-mentioned macromolecular monomer, styrene and methyl methacrylate were used at a weight ratio of 70:18:12. There was also used 8.4 mole %, based on the total moles of the above polymerizable components, of AIBN as a polymerization initiator. They were subjected to polymerization reaction in toluene at 60°C for 8 hours.

15 The resulting branched-chain polymer was made into a toluene solution containing 20% by weight of the polymer. To 50 parts by weight of the solution (containing 10 parts by weight of the polymer; the amount of sulfur atom contained in the polymer = 8.05 mM) was added 15 parts by weight of m-chloroperbenzoic acid (purity = 80%) (the amount of m-chloroperbenzoic acid = 69.5 mM), and the mixture was subjected to reaction at 20°C for 3 hours.

25 In the course of the reaction, the amount of the peroxide in the reaction mixture was determined by iodometry. When the amount became constant, the reaction was stopped. The subsequent procedure was carried out similarly to the above Examples to remove the residual

- 1 peroxide and obtain a branched-chain polymer after
oxidation treatment.

The polymer was measured for (1) weight-average
molecular weight by small-angle light-scattering photo-
5. metry and (2) solution viscosity (viscosity of acetone
solution containing 40% by weight of a polymer, at 25°C
as measured using Ubbellohde viscometer; this applies to
the solution viscosity of Example 9). The results were
as follows.

10

Mw: 23,100

η : 13.2 (cp)

The polymer was also evaluated for weather-
ability. As a result, the film of the polymer gave no
yellowing.

15 Example 7

The branched-chain polymer obtained by the
polymerization of Example 6 was oxidized with hydrogen
peroxide.

To 50 parts by weight of a toluene solution
20 containing 20% by weight of the above polymer (containing
10 parts by weight of the polymer; the amount of sulfur
atom contained in the polymer = 8.05 mM) was added 4.86
parts by weight of an aqueous hydrogen peroxide solution
(35% concentration) (50.08 mM). The mixture was subjected
25 to reaction at 60°C for 16 hours. In the course of the
reaction, the amount of hydrogen peroxide in the reaction
mixture was determined by iodometry. When the amount

1 became constant, the reaction was stopped.

A polymer after oxidation treatment was separated from the reaction mixture and evaluated for weatherability. As a result, the film of the polymer
5 gave no yellowing.

Example 8

The same procedure as in Example 7 was repeated except that 0.058 parts by weight of phosphotungstic acid was used as a catalyst in the oxidation reaction. The
10 oxidation reaction was finished in 8 hours.

The polymer after oxidation was evaluated for weatherability. The result was good similarly to that in Example 7.

Example 9

15 93% by weight of the macromolecular monomer synthesized in Example 6 and 7% by weight of styrene were copolymerized as follows.

The above two components were reacted in toluene at 60°C for 8 hours using AIBN as a polymeriza-
20 tion initiator and lauryl mercaptan as a chain transfer agent in amounts of 8.4 mole % and 7.5 mole %, respectively, based on the total moles of the two components.

10 parts by weight of the resulting polymer (the amount of sulfur atom in the polymer = 10.7 mM) and
25 92.7 mM of m-chloroperbenzoic acid were subjected to oxidation reaction in the same manner as in Example 6.

- 1 The resulting polymer had the following weight-average molecular weight and solution viscosity.

Mw: 19,000

η : 11.4 (cp)

- 5 The polymer was also evaluated for weatherability. As a result, the film of the polymer gave no yellowing and had good weatherability.

CLAIMS

1. A process for producing a polymer, _____ which comprises reacting a polymer having a thioether bond with a peroxide to oxidize the sulfur atom in the thioether bond to convert it into a sulfone.

2. A process according to Claim 1, wherein the polymer having a thioether bond is a straight-chain or branched-chain (meth)acrylic acid ester polymer having a number-average molecular weight of 500-20,000.

3. A process according to either of Claims 1 and 2, wherein the peroxide is selected from _____ perbenzoic acid, m-chloroperbenzoic acid, peracetic acid, perhexanoic acid, tert-butyl hydroperoxide, cumene hydroperoxide, hydrogen peroxide, potassium persulfate, oxone, magnesium monoperoxyphthalate and ozone, and the peroxide is used in an amount which is at least twice the equivalent of _____ thioether bond contained in the polymer to be oxidized.

4. A process for producing a macromolecular monomer, _____ which comprises:

[a] polymerizing at least one ethylenically unsaturated monomer in the presence of a mercaptan having a thiol group and a reactive group in the molecule,

[b] reacting the polymer obtained in _____ [a] with a peroxide to oxidize the sulfur atom in the thioether bond present in the polymer to convert

it into a sulfone, and

[c] reacting the polymer obtained in _____ [b] with a compound having a functional group which is addition-reactive with the reactive group present at one end of the polymer, and an ethylenically unsaturated bond, to obtain the macromolecular monomer.

5. A process according to Claim 4, wherein the mercaptan having a thiol group and a reactive group in the molecule is selected from _____ mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid and 2-mercaptoethanol.

6. A process according to either of Claims 4 and 5, wherein the monomer used in [a] is selected from _____ methyl (meth)acrylate, ethyl (meth)-acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, (meth)acrylonitrile, styrene and α -methylstyrene.

7. A process according to any one of Claims 4 to 6, wherein the peroxide is selected from _____ perbenzoic acid, m-chloroperbenzoic acid, peracetic acid, perhexanoic acid, tert-butyl hydroperoxide, cumene hydroperoxide, hydrogen peroxide, potassium persulfate, oxone, magnesium monoperoxyphthalate and ozone and the peroxide is used in an amount which is at least twice the equivalent of thioether bond contained in the polymer to be oxidized.

8. A process according to any one of Claims 4 to 7, wherein the

compound having a functional group and an ethylenically unsaturated bond used in _____ [c] is selected from _____ glycidyl methacrylate, glycidyl acrylate, methacrylic acid chloride, p-vinylbenzyl chloride and p-vinyllaniline.

9. A process for producing a branched-chain polymer, _____ which comprises copolymerizing the macromolecular monomer obtained by the process of any one of Claims 4 to 8 with another monomer.

10. A process according to Claim 9, wherein the monomer to be copolymerized with the macromolecular monomer is selected from _____ alkyl (C₁-C₁₈) (meth)acrylates, perfluoroalkyl (C₁-C₁₈) (meth)acrylates, styrene, (meth)acrylonitrile, (meth)acrylic acid, maleic anhydride, 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, glycidyl (meth)acrylate, N-methylolacrylamide, N,N-dimethylamino ethyl (meth)acrylate and (meth)acryloyloxypropyl-trimethoxysilane.

11. A process for producing a branched-chain polymer, _____ which comprises :

[d] polymerizing an ethylenically unsaturated monomer in the presence of a mercaptan having a thiol group and a reactive group in the molecule,

[e] reacting the polymer obtained in _____ [d] with a compound having a functional group which is addition-reactive with the reactive group

present at one end of the polymer, and an ethylenically unsaturated bond, to obtain a macromolecular monomer,

[f] copolymerizing the macromolecular monomer having an ethylenically unsaturated bond at one end of the molecule obtained —————[e] with another monomer to synthesize a branched-chain polymer, and

[g] reacting the branched-chain polymer obtained in —————[f] with a peroxide to oxidize the sulfur atom in the thioether bond present in the branched-chain polymer to convert it into a sulfone.

12. A process according to Claim 11, wherein the mercaptan having a thiol group and a reactive group in the molecule is selected from ————— mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid and 2-mercaptoethanol.

13. A process according to either of Claims 11 and 12, wherein the monomer used in [d] is selected from ————— methyl (meth)acrylate, ethyl (meth)-acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, (meth)acrylonitrile, styrene and α -methylstyrene.

14. A process according to any one of Claims 11 to 13, wherein the compound having a functional group and an ethylenically unsaturated bond, used in ————— [e] is selected from ————— glycidyl methacrylate, glycidyl acrylate, methacrylic acid chloride, p-vinylbenzyl chloride and p-vinyllaniline.

15. A process according to any one of Claims 11 to 14, wherein the

monomer to be copolymerized with the macromolecular monomer is selected from alkyl (C₁-C₁₈) (meth)acrylates, perfluoroalkyl (C₁-C₁₈) (meth)acrylates, styrene, (meth)acrylonitrile, (meth)acrylic acid, maleic anhydride, 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, glycidyl (meth)acrylate, N-methylolacrylamide, N,N-dimethylamino ethyl (meth)acrylate and (meth)acryloyloxypropyl-trimethoxysilane.

16. A process according to any one of Claims 11 to 15, wherein the peroxide is selected from perbenzoic acid, m-chloroperbenzoic acid, peracetic acid, perhexanoic acid, tert-butyl hydroperoxide, cumene hydroperoxide, hydrogen peroxide, potassium persulfate, oxone, magnesium monoperoxyphthalate and ozone and the peroxide is used in an amount which is at least twice the equivalent of thioether bond contained in the polymer to be oxidized.

17. A solvent-based coating composition containing a polymer obtainable by the process of any preceding Claim.

18. A polymer obtainable by the process of any preceding Claim.

19. An article coated with the composition of Claim 17.

20. A process according to Claim 1 substantially as hereinbefore described.

21. A process according to Claim 4 substantially as hereinbefore described.

22. A process according to Claim 9 substantially as hereinbefore described.

23. A process according to Claim 11 substantially as hereinbefore described.

24. A solvent-based coating composition according to Claim 17

substantially as hereinbefore described.

25. A polymer according to Claim 18 substantially as hereinbefore described.

5

26. An article according to Claim 19 substantially as hereinbefore described.

**Examiner's report to the Comptroller under
Section 17 (The Search Report)**

GB 9302603.7

Relevant Technical fields

(i) UK Cl (Edition L) C3J (JAK) C3P (PDIF)

(ii) Int Cl (Edition 5) C08F

Search Examiner

K MACDONALD

Databases (see over)

(i) UK Patent Office

(ii)

Date of Search

1 APRIL 1993

Documents considered relevant following a search in respect of claims 1-26

| Category (see over) | Identity of document and relevant passages | Relevant to claim(s) |
|------------------------|--|-------------------------|
| X | GB 1526301 (CIBA-GEIGY) - Claims 12, 20, 23, 24 | at least Claim 1 |
| X | GB 1283087 (UNIROYAL) - page 6, lines 8-20 | at least Claim 1 |
| X | EP 0096459 A2 (ICI) - eg Step 2 on page 4 | at least Claim 1 |

| Category | Identity of document and relevant passages | Relevant to claim(s) |
|----------|--|----------------------|
| | | |

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).